

Introduction to Phase Diagrams*

IN MATERIALS SCIENCE, a phase is a physically homogeneous state of matter with a given chemical composition and arrangement of atoms. The simplest examples are the three states of matter (solid, liquid, or gas) of a pure element. The solid, liquid, and gas states of a pure element obviously have the same chemical composition, but each phase is obviously distinct physically due to differences in the bonding and arrangement of atoms.

Some pure elements (such as iron and titanium) are also *allotropic*, which means that the crystal structure of the solid phase changes with temperature and pressure. For example, iron undergoes several distinct solid-state changes of its crystal structure with temperature. Alloying, the formation of a substance with metallic properties composed of two or more elements, also affects the occurrence of phase changes. For example, the temperature for complete melting (100% liquid phase) of an alloy depends on the relative concentration of alloying elements. Alloying also affects the stable crystalline phase of a solid. Depending on how two or more elements behave when mixed, the elements may form different crystalline phases and/or chemical compounds.

Phase diagrams and the systems they describe are often classified based on the number of components (typically elements) in the system (Table 1). A unary phase diagram plots the phase changes of one element as a function of temperature and pressure. A binary diagram plots the phase changes as a function of temperature for

a system with varying composition of two components. While other extensive and intensive properties influence the phase structure, materials scientists typically hold these properties constant for practical ease of use and interpretation. Phase diagrams are usually constructed with a constant pressure of one atmosphere.

Phase diagrams are useful graphical representations that show the phases in equilibrium present in the system at various specified compositions, temperatures, and pressures. It should be recognized that phase diagrams represent equilibrium conditions for an alloy, which means that very slow heating and cooling rates are used to generate data for their construction. The equilibrium states that are represented on phase diagrams are known as *heterogeneous equilibria*, because they refer to the coexistence of different states of matter (gas, liquid, and/or solid phases with different crystal structures). When two or more phases are in mutual equilibrium, each phase must be in the lowest free-energy state possible under the restrictions imposed by its environment. This equilibrium condition means that each phase is in an internally homogeneous state with a chemical composition that is identical everywhere within each phase, and that the molecular and atomic species of which the phase is composed (if more than one) must be present in equilibrium proportions.

Because industrial practices almost never approach equilibrium, phase diagrams should be used with some degree of caution. Kinetic effects, including surface energies, activation energies, and diffusion and reaction rates, affect the time needed to initiate and complete a physical or chemical phase change. With rapid heating, any phase change, such as melting, occurs at a slightly higher temperature than with slow heating. Conversely, with rapid cooling, the phase change occurs at a lower temperature than with slow cooling. Therefore, transformations observed during heating are at higher temperatures than the reverse transformations observed during cooling, except in the hypothetical case wherein the rates of heating and cooling are infinitely slow, where the two observations of temperature would coincide at the equilibrium transformation temperature.

Nevertheless, phase diagrams are instrumental in predicting phase transformations and their resulting microstructures. True equilibrium is, of course, rarely attained by metals and alloys in the course of ordinary manufacture and application. Rates of heating and cooling are usually too fast, times of heat treatment too short, and phase changes too sluggish for the ultimate equilibrium state to be reached. However, any change that does occur must constitute an adjustment toward equilibrium. Hence, the direction of change can be ascertained from the phase diagram, and a wealth of experience is available to indicate the probable degree of attainment of equilibrium under various circumstances. As such, alloy phase diagrams are useful to metallurgists, materials engineers, and materials scientists in four major areas:

- Development of new alloys for specific applications
- Fabrication of these alloys into useful configurations
- Design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties
- Solving problems that arise with specific alloys in their performance in commercial applications

Unary Systems

A system containing only one pure metal is referred to as a unary system, which can exist as a solid, liquid, and/or gas, depending on the specific combination of temperature and pressure. Assuming a constant atmospheric pressure, a metal melts when heated to a specific temperature and boils with further heating to a specific boiling temperature. Through evaporation, metal atoms leave the container as a vapor. In conditions where matter can enter or leave the system, these systems are known as open systems.

To create a closed system where no matter enters or leaves the system, an airtight cover can be placed on top of the container. If pressure is held constant during boiling, then an

Table 1 Terminology for the number of elements in an alloy phase diagram

Number of components	Name of system or diagram
One	Unary
Two	Binary
Three	Ternary
Four	Quaternary
Five	Quinary
Six	Sexinary
Seven	Septenary
Eight	Octanary
Nine	Nonary
Ten	Decinary

* Adapted from F.C. Campbell, Ed., *Phase Diagrams: Understanding the Basics*, ASM International, 2012, and H. Baker, Alloy Phase Diagrams and Microstructure, *Metals Handbook Desk Edition*, ASM International, 1998, p 95–114.

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increase in volume of the closed system must occur. Conversely, if pressure is increased, the vapor phase is compressed and the volume of the vapor becomes smaller. The volume of liquid metal remains fairly constant with the application of pressure; that is, liquid metals are essentially incompressible. The same situation holds if the liquid metal is cooled so that only a solid remains. Metal atoms in a liquid state are almost as closely packed as they are in the solid state, so the effects of pressure and volume change can often be approximated as statistically negligible.

All pure metals have a unique melting point. Metals with weak interatomic bonds melt at lower temperatures. This includes several soft metals such as lead, tin, and bismuth. In contrast, the refractory metals have high melting points. The refractory metals include niobium, tantalum, molybdenum, tungsten, and rhenium. A two-phase system exists when a container consists of both a liquid phase and a vapor phase. In this example, a liquid is in equilibrium with its vapor phase, when the average rate of atoms leaving the liquid equals the rate joining the liquid from the gas. If pressure is increased, the result is fewer atoms in the gas phase and more in the liquid phase, and the ratio of atoms in each phase remains constant once equilibrium (constant temperature and pressure) is reestablished.

Solid-State Crystal Structures

The solid state of a unary system involves bonding of adjacent atoms in different arrangements. Atoms in some solids have an amorphous structure, which is an arrangement without a pattern or periodic structure. Atoms in solids usually form a crystal structure, which is a *repetitive and symmetrical* arrangement of atoms in three dimensions. Metal atoms, for example, tend to form crystal structures due to the nature of metallic bonding. Metals are atoms with an outermost electron shell that has a spherically shaped electron cloud with a valence electron. The metallic bond occurs when valence electrons are shared amongst the metal atoms in the matrix, and the type of crystal structure is influenced by the nature of the electron cloud in the outer shell.

The crystal structure depends on the type of bonding (ionic, covalent, metallic) between atoms in a solid. The Periodic Table of elements in Fig. 1 identifies the crystal structures of the various metallic elements. The most common crystal structures of the metallic elements (Fig. 2) are face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp).

Crystals have been classified into seven basic systems (see the appendix “Crystal Structure” in this Volume). Six of the seven crystal systems also can occur with one of five different lattice arrangements of atoms, such that the same kind of atom (or a group of atoms in a compound) of identical composition occurs in a periodic array of points (lattice points) in space. In effect, there

are 14 kinds of space lattices, derived from all the possible varieties of interatomic spacing, lattice arrangements, and interaxial angles within the seven crystal systems.

Polymorphism and Allotropy

Some elements and compounds exhibit more than one stable solid crystalline phase dependent on temperature and pressure; these materials are called *polymorphic*, or *allotropic* for pure elements.

The most commonly used allotropic element is iron, which undergoes a series of phase transformations as a function of temperature and pressure (Fig. 3). At room temperature, iron has a bcc structure (also known as ferrite, or α iron). Ferrite is ferromagnetic at room temperature, but if temperature is slowly increased, α ferrite becomes paramagnetic at the Curie temperature of 770 °C (1418 °F). When temperature is increased further, the paramagnetic ferrite changes to an fcc crystal structure referred to as austenite or γ iron. Austenite is completely paramagnetic. At higher temperatures, austenitic iron changes to a high-temperature bcc structure, referred to as δ iron. Similar phase changes occur during cooling. Under equilibrium conditions, the solidification of pure iron from the liquid occurs at 1540 °C (2800 °F) and forms δ iron. Delta iron is then stable on further cooling until it reaches approximately 1390 °C (2541 °F), where it undergoes a transformation to an fcc structure of austenite (γ iron). On still further cooling, austenite changes into the bcc structure of ferrite (α iron). This last transformation is extremely important because it forms the basis for the hardening of steel. Also, it should be noted (as in the previous example of transformation from δ iron to γ iron) that the temperatures of transformation during cooling may be slightly lower than the temperatures of transformation during heating (Fig. 3). This temperature differential is known as the temperature hysteresis of allotropic phase transformation, and its magnitude increases with increases in the cooling rate. Very slow heating or cooling approaches equilibrium conditions, in which case transformation temperatures would be essentially the same for heating and cooling.

When any phase transformation occurs during slow heating or cooling, there is an arrest or plateau in the temperature change during transformation. That is, temperature remains constant at the critical temperature for some period until the phase change is complete for all the matter in the system. At the transformation temperature, the process of transformation continues with any addition or extraction of thermal energy. After transformation is complete, then slow heating or cooling results in a temperature change of the system.

In the case of iron (and also steel as an iron-carbon alloy), the critical temperatures for phase transformation are assigned the letter *A*, derived from the French word *arrêt* that stands

for the “arrest” in temperature during heating or cooling through the transformation temperature. The letter *A* also is followed by the letter *c* or *r* to indicate transformation by either heating or cooling, respectively. The use of letter *c* for heating is derived from the French word *chauffant*, meaning warming. If cooling conditions apply, the critical temperature is designated as “Ar,” with the letter *r* being derived from the French word *refroidissant* for cooling.

Many other metals and nonmetals also exhibit allotropic transformations (Table 2). For example, titanium, zirconium, and hafnium all exhibit a transition from an hcp structure to bcc on heating. Note that in each case, a close-packed structure is stable at room temperature, while a looser packing is stable at elevated temperatures. While this is not always the case, it is a trend experienced with many metals.

Binary Systems

A binary phase diagram plots the different states of matter as a function of temperature for a system at constant pressure with varying composition of two components (or elements). The addition of an alloying element represents another degree of freedom (or variable), which thus allows two distinct forms (or phases) to coexist under equilibrium conditions. The mixed (i.e., heterogeneous) equilibria phases in binary alloys also can occur in either solids or when liquid and solid phases change during melting or solidification, as described in the following sections. (See also the section “The Gibbs Phase Rule” in this article on the variables affecting heterogeneous phase equilibria).

In many industries, alloy composition is normally expressed in weight percentage, but for certain types of scientific work the atomic percentage scale may be preferred. If desired, composition may also be given in terms of the percentage by volume, but this usage is rare in the representation of metal systems.

The conversion between weight percentage (wt%) and atomic percentage (at.%) may be accomplished in a binary system by the use of the formulas:

$$\text{wt\% A} = \frac{\text{at.\% A} \cdot \text{at.wt of A}}{(\text{at.\% A} \cdot \text{at.wt of A}) + (\text{at.\% B} \cdot \text{at.wt of B})} \cdot 100 \quad (\text{Eq 1})$$

and

$$\text{at.\% A} = \frac{\text{wt\% A/at.wt of A}}{(\text{at.\% A/at.wt of A}) + (\text{wt\% B/at.wt of B})} \cdot 100 \quad (\text{Eq 2})$$

The equation for converting from atomic percentages to weight percentages in higher-order systems is similar to that for binary systems, except that an additional term is added to the denominator for each additional component. For example, for ternary systems:

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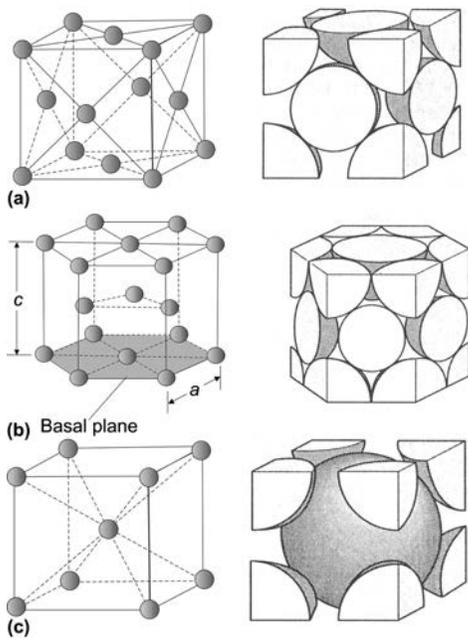


Fig. 2 Arrangement of atoms: (a) face-centered cubic (fcc), (b) hexagonal close-packed (hcp), and (c) body-centered cubic (bcc) crystal structures. Source: Ref 2

$$\text{at.\% A} = \frac{\text{wt\% A/at.wt of A}}{(\text{at.\% A/at.wt of A}) + (\text{wt\% B/at.wt of B}) + (\text{wt\% C/at.wt of C})} \cdot 100 \quad (\text{Eq 3})$$

$$\text{wt\% A} = \frac{\text{at.\% A} \cdot \text{at.wt of A}}{(\text{at.\% A} \cdot \text{at.wt of A}) + (\text{at.\% B} \cdot \text{at.wt of B}) + (\text{at.\% C} \cdot \text{at.wt of C})} \cdot 100 \quad (\text{Eq 4})$$

where A, B, and C represent the metals in the alloy.

Effect of Alloying on Melting/Solidification

Binary systems have two elements of varying concentration. Unlike pure metals, alloys do not necessarily have a unique melting point. Instead, most alloys have a *melting range*. This behavior can be seen in the phase diagram for copper-nickel (Fig. 4). The *solidus line* is where the solid phase begins to melt, and the new phase consists of a mixture of a solid-solution phase and some liquid phase. This solid-liquid mix in a two-phase region is referred to as the *mushy zone*. Like the two-phase system of a liquid and vapor phase in a closed system, the liquid phase is in equilibrium with the solid when the average rate of atoms leaving the liquid equals the rate joining the liquid from the solid phase. Temperature and alloy concentration changes the relative amount of liquid and solid phase in the mushy zone (see the section “The Lever Rule” in this article).

The reason for the mushy zone can be understood in qualitative terms by examining the

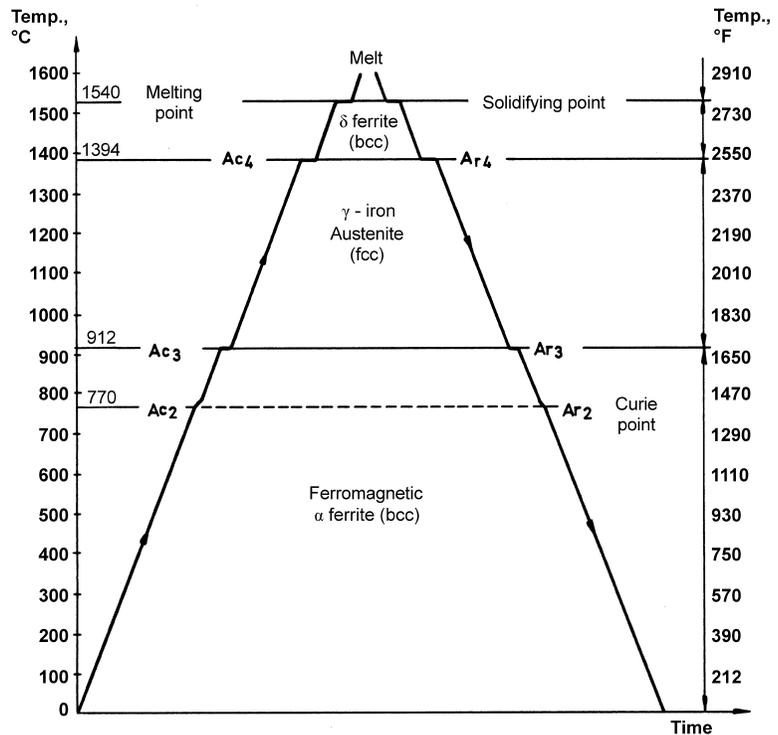


Fig. 3 Phase changes of pure iron with very slow (near equilibrium) heating and cooling. When heating, the critical temperatures of phase change are designated as Ac_2 , Ac_3 , and Ac_4 . Because some hysteresis occurs (depending on the rate of heating or cooling), critical temperatures of phase change during cooling are designated as Ar_2 , Ar_3 , and Ar_4 . If critical temperatures are determined under equilibrium conditions, the designations of critical temperatures are Ae_2 , Ae_3 , and Ae_4 . Source: Ref 2

nickel-copper phase diagram (Fig. 4). Pure copper has a lower melting point than nickel. Therefore, in a nickel-copper alloy, the copper atoms melt before the regions rich in nickel. The mushy zone becomes 100% liquid when the temperature is raised above the *liquidus line*. As one might expect, the liquidus line converges to the melting points of the pure metals in an alloy phase diagram. The liquidus denotes for each possible alloy composition the temperature at which freezing begins during cooling or, equivalently, at which melting is completed on heating.

The lower curve, called the *solidus*, indicates the temperatures at which melting begins on heating or at which freezing is completed on cooling. Above the liquidus every alloy is molten, and this region of the diagram is, accordingly, labeled *L* for the liquid phase or liquid solution. Below the solidus all alloys are solid, and this region is labeled α because it is customary to use Greek letters to designate different solid phases. At temperatures between the two curves, the liquid and solid phases both are present in equilibrium, as is indicated by the designation $L + \alpha$.

However, it also is important to understand that *some specific alloy compositions do not* have a mushy zone. That is, some alloys have a unique composition with a specific melting point that is *lower* than the melting points of the two pure metals in the alloy! This type of

alloy is referred to as a *eutectic alloy* (where the term *eutectic* is taken from the Greek word for “easily melted”).

Eutectic systems are described in more detail in the article “Eutectic Alloy Systems” in this Volume. Eutectic alloys are important because complete melting occurs at a low temperature. For example, cast irons are based on compositions around the iron-carbon eutectic composition of iron with 4.30 wt% C (Fig. 5). This improves castability by lowering the temperature required for melting and also promotes better solidification during casting. Another industrially significant eutectic is in the lead-tin system for solders.

Effect of Alloying on Solid-State Transformations

When small amounts of another element are added to a pure metal, some (or all) of the alloying element can be accommodated (dissolved) within the solid crystal matrix of the parent metal (see the article “Solid Solutions and Phase Transformations” in this Volume). This dissolution of the element within the crystal matrix of solid metal is referred to as a *solid solution*. The parent metal is referred to as the *solvent*, while the alloying element is referred to as the *solute*. The phase structure of a solid solution is the same as that of the parent metal.

There are limits to the solid solubility of one element in another, depending on the similarity and differences of the two atoms. For example, nickel and copper are very similar. Both have

the fcc crystalline structure and the atoms are of roughly similar size. Thus, the elements are completely miscible, and the nickel-copper system consists of one solid phase (α) below the

solidus line (Fig. 4). This type of system is referred to as isomorphous system, which is described in more detail in the article “Isomorphous Alloy Systems” in this Volume.

More complex behavior occurs when alloying elements have significantly dissimilar atomic sizes and different crystalline structures than that of the parent matrix. When the host (solvent) lattice cannot dissolve any more solute atoms, the excess solute may group together to form a separate distinct phase. Excess solute atoms can also react with solvent atoms to form an *intermetallic* compound (which is a phase with a crystal structure different from that of either pure metal). For example, when the level of carbon exceeds its solubility limit in iron, the excess carbon not dissolved in the iron gets tied up in separate phases of a metastable intermetallic compound, Fe_3C , called *cementite*.

The iron-carbon phase diagram (Fig. 5) also makes a distinction between phase boundaries for iron-carbon and iron carbide (Fe_3C). In actuality, cementite (Fe_3C) is not a true equilibrium phase in the iron-carbon system and is referred to as metastable. Over a long exposure time (depending on temperature), cementite eventually decomposes into iron and free carbon (graphite). However, the rate of decomposition of iron carbide is extremely slow under the most favorable conditions and is usually imperceptible under ordinary conditions for the applications designed.

Because of its reluctance to decompose, the metastable cementite phase is represented on the iron-carbon phase diagram as a phase that is *approximately* in stable equilibrium in most practical circumstances. The iron-cementite phase diagram is important to industrial metallurgy, especially in the solid-state heat treatment of steel. However, the development of an iron-base microstructure with graphite (in the shape of flakes or nodules) is important in the production of cast irons. These alloys contain silicon additions as a catalyzing substance that helps

Table 2 Solid-state allotropes in selected metals

Element	Structure	Temperature range	
		°C	°F
Beryllium	hcp	<1250	<2280
	bcc	>1250	>2280
Calcium	fcc	<450	<840
	bcc	>450	>840
Cerium	hcp	-150 to -10	-238 to -14
	fcc	-10 to 725	-14 to 1340
	bcc	>725	>1340
Cobalt	hcp	<425	<795
	fcc	Quenched from >450	Quenched from >840
Dysprosium	hcp	<1381	<2520
	bcc	>1381	>2520
Gadolinium	hcp	<1264	<2310
	bcc	>1264	>2310
Hafnium	hcp	<1950	<3540
	bcc	>1950	>3540
Holmium	hcp	<906	<1660
	?	>906	>1660
Iron	bcc	<910	<1670
	fcc	910 to 1400	1670 to 2550
	bcc	>1400	>2550
Lanthanum	hcp	-271 to 310	-455 to 590
	fcc	310 to 868	590 to 1590
	bcc	>868	>1590
Lithium	hcp	<-202	<-330
	bcc	>-202	>-330
Lutetium	hcp	<1400	<2550
	?	>1400	>2550
Manganese	Four cubic phases
Mercury	bct	<-194	<-317
	Rhombohedral	>-194	>-317
Neodymium	hcp	<868	<1590
	bcc	>868	>1590
Neptunium	Orthorhombic	<280	<535
	Tetragonal	280 to 577	535 to 1070
	bcc	577 to 637	1070 to 1180
Plutonium	Several phases
Polonium	Simple cubic	>76	>169
	Rhombohedral
Praseodymium	hcp	<798	<1470
	bcc	>798	>1470
Samarium	Rhombohedral	<917	<1680
	bcc	>917	>1680
Scandium	hcp	<1000 to 1300	<1830 to 2370
	bcc	>1335	>2440
Sodium	hcp	<237	<460
	bcc	>237	>460
Strontium	fcc	<540	<1000
	bcc	>540	>1000
Terbium	hcp	<1317	<2400
	bcc	>1317	>2400
Thallium	hcp	<230	<445
	bcc	>230	>445
Titanium	hcp	<885	<1630
	bcc	>885	>1630
Uranium	Orthorhombic	<662	<1220
	Tetragonal	662 to 774	1220 to 1430
	bcc	774 to 1132	1430 to 2070
Ytterbium	fcc	RT to 798	RT to 1470
	bcc	>798	>1470
Yttrium	hcp	RT to 1460	RT to 2660
	bcc	>1460	>2660
Zirconium	hcp	<865	<1590
	bcc	>865	>1590

Summary:

- In 14 metals, hcp transforms to bcc as temperature increases.
- In 3 metals, hcp transforms to fcc as temperature increases.
- In 6 metals, fcc transforms to bcc as temperature increases.
- In 0 metals, fcc transforms to hcp as temperature increases.
- In 0 metals, bcc transforms to hcp as temperature increases.
- In 1 metal, bcc transforms to fcc as temperature increases.

hcp, hexagonal close-packed; bcc, body-centered cubic; fcc, face-centered cubic; bct, body-centered tetragonal; RT, room temperature

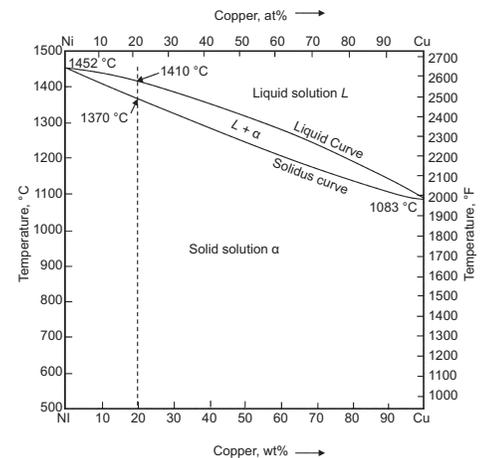


Fig. 4 The nickel-copper phase diagram. Adapted from Ref 3

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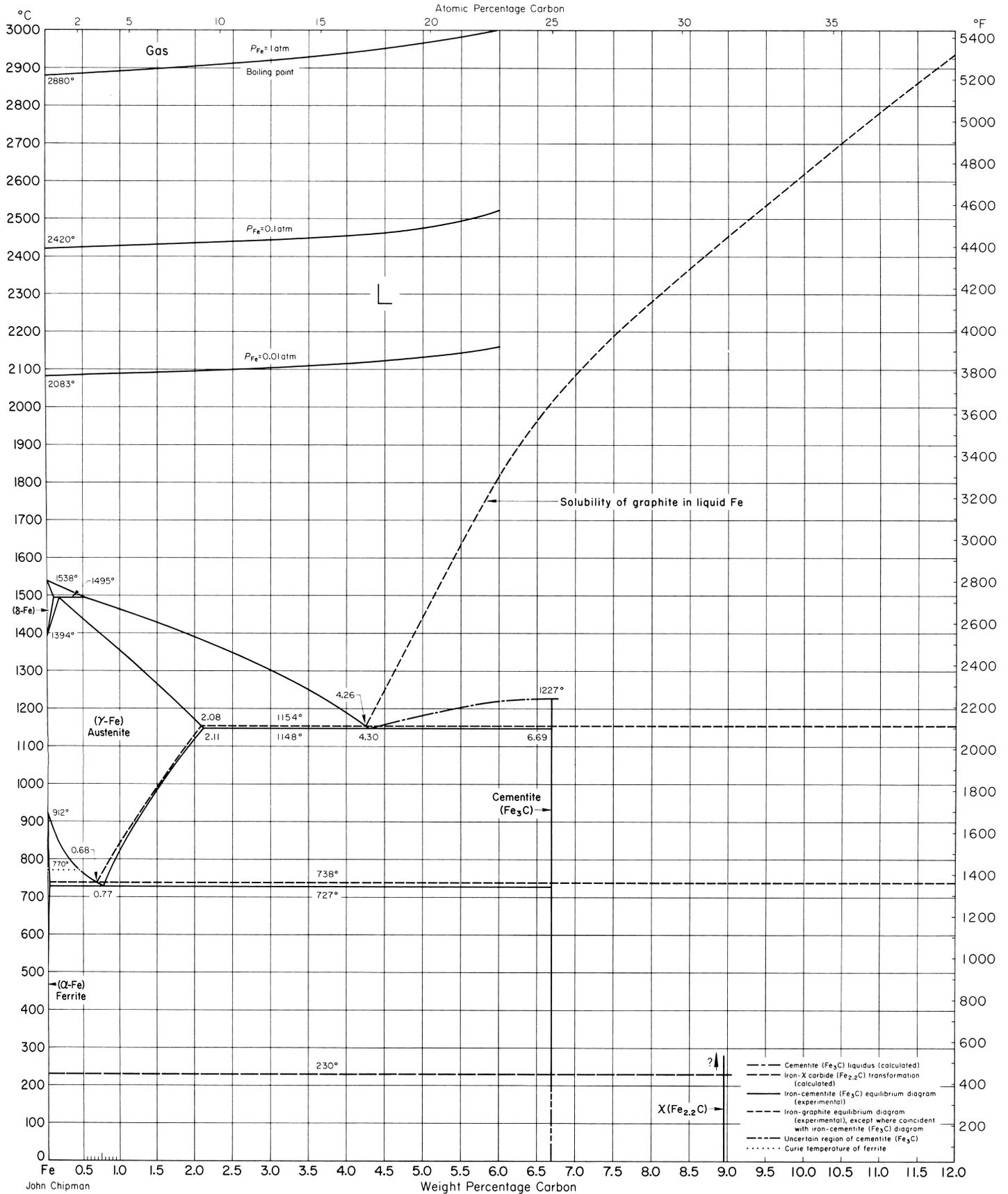


Fig. 5 Iron-carbon phase diagram with constituents in the form of cementite (Fe_3C) and graphite (as the equilibrium form of carbon). Although cementite is strictly a metastable phase that eventually decomposes into iron and graphite, cementite is sufficiently stable over the time scales of most engineering applications.

breaks down iron carbides to produce iron and free carbon as graphite during solidification.

In addition, the iron-carbon phase diagram also illustrates the coexistence of two solid-state phases in several areas. One area of heterogeneous phase equilibria is the indicated region of ferrite (α iron) and austenite (γ iron). At lower concentrations of carbon and high enough temperatures, a two-phase region of solid α iron and solid γ iron in equilibrium forms. Another two-phase region of solid iron exists with γ iron and δ iron at higher temperatures. These regions are the solid-state analog of the two-phase (mushy) zone that occurs on melting or solidification.

Ternary Diagrams

When more than two components exist in a system, illustrating equilibrium conditions graphically in two dimensions becomes more complicated. One option is to add a third composition dimension to the base, forming a solid diagram having binary diagrams as its vertical sides. This can be represented as a modified isometric projection, such as shown in Fig. 6. Here, boundaries of single-phase fields (liquidus, solidus, and solvus lines in the binary diagrams) become surfaces; single- and two-phase areas become volumes; three-phase lines become volumes; and four-phase points, while not shown in Fig. 6, can exist as an invariant plane. The composition of a binary eutectic liquid, which is a point in a two-component system, becomes a line in a ternary diagram, as shown in Fig. 6.

While three-dimension projections can be helpful in understanding the relationships in the diagram, reading values from them is difficult. In order to represent three dimensions on two-dimensional diagrams, pressure and temperature are typically fixed. Ternary systems are often represented by views of the binary diagrams that comprise the faces and two-dimensional projections of the liquidus and solidus surfaces, along with a series of two-dimensional horizontal sections (*isotherms*) and vertical sections (*isopleths*)

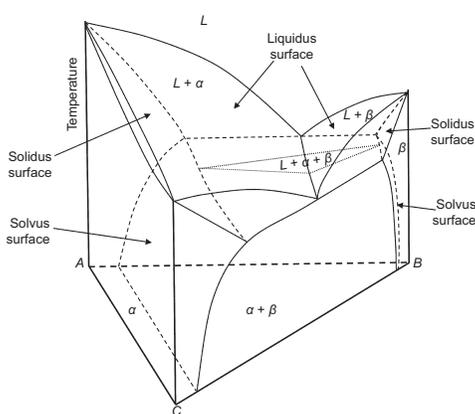


Fig. 6 Ternary phase diagram showing three-phase equilibrium. Adapted from Ref 3

through the solid diagram. See the article “Introduction to Ternary Diagrams” in this Volume for more details.

Isothermal Sections. Composition values in the triangular isothermal sections are read from a triangular grid consisting of three sets of lines parallel to the faces and placed at regular composition intervals (see Fig. 7a). Normally, the point of the triangle is placed at the top of the

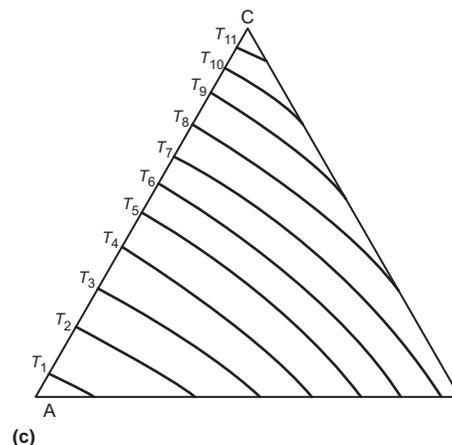
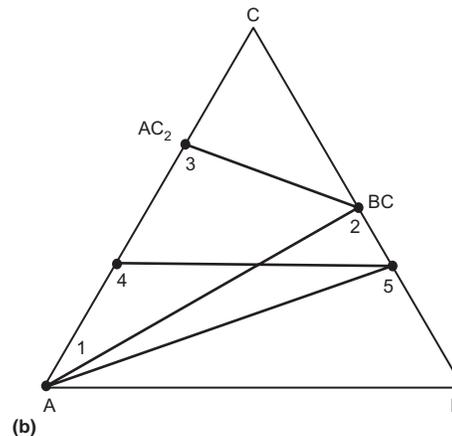
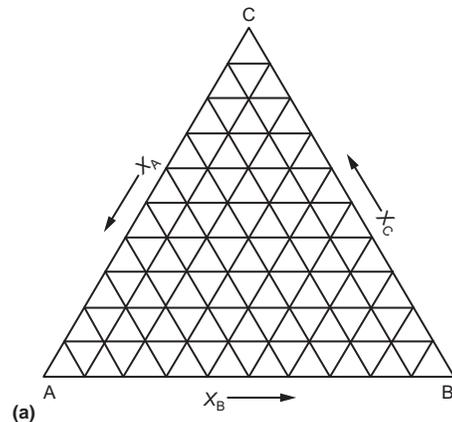


Fig. 7 Two-dimensional projections from a ternary phase diagram. (a) Isothermal section. (b) Vertical section. (c) Isothermal contours for a liquidus or solidus projection

illustration, component A is placed at the bottom left, B at the bottom right, and C at the top. The amount of constituent A is normally indicated from point C to point A, the amount of constituent B from point A to point B, and the amount of constituent C from point B to point C. This scale arrangement is often modified when only a corner area of the diagram is shown.

Vertical sections are often taken through one corner (one component) and a congruently melting binary compound that appears on the opposite face; when such a plot can be read like any other true binary diagram, it is called a *quasi-binary* section. An example of such a section is illustrated by line 1–2 in the isothermal section shown in Fig. 7(b). A vertical section between a congruently melting binary compound on one face and one on a different face might also form a quasi-binary section (see line 2–3).

All other vertical sections are not true binary diagrams, and the term *pseudobinary* is applied to them. A common pseudobinary section is one where the percentage of one of the components is held constant (the section is parallel to one of the faces), as shown by line 4–5 in Fig. 7(b). Another is one where the ratio of two constituents is held constant, and the amount of the third is varied from 0 to 100% (line 1–5).

Projected Views. Liquidus, solidus, and solvus surfaces by their nature are not isothermal. Therefore, equal-temperature (isothermal) contour lines are often added to the projected views of these surfaces to indicate the shape of the surfaces (see Fig. 7c). In addition to (or instead of) contour lines, views often show lines indicating the temperature troughs (also called valleys or grooves) formed at the intersections of two surfaces. Arrowheads are often added to these lines to indicate the direction of decreasing temperature in the trough.

Phase Diagrams Rules and Notation

The construction of phase diagrams is greatly facilitated by certain rules that come from thermodynamics. Foremost among these is the second law of thermodynamics and the Gibbs phase rule, which leads to rules governing the construction of more complex phase diagrams (for more details see the article “Thermodynamics and Phase Diagrams” in this Volume).

The term *phase* is based on the work of the American mathematician Josiah Willard Gibbs (Ref 4), who first introduced the term in describing the thermodynamics of heterogeneous solids. Solids may have a homogenous structure, such that the alloying elements (or components) arrange themselves into a repeatable type of crystal structure. However, solids do not always have a homogenous structure of the constituent atoms. Many solids are heterogeneous—that is, the atomic elements can arrange themselves into more than one type of structure under equilibrium conditions.

The Gibbs Phase Rule

The construction of phase diagrams is greatly facilitated by certain rules that come from thermodynamics. Foremost among these is Gibbs' phase rule, which applies to all states of matter (solid, liquid, and gaseous) under equilibrium conditions. The maximum number of phases (P) that can coexist in a chemical system, or alloy, is:

$$P = C - F + 2 \quad (\text{Eq 5})$$

where F is the number of degrees of freedom, and C is the number of chemical components (usually elements for alloys). The phases are the homogeneous parts of a system that, having definite bounding surfaces, are conceivably separable by mechanical means alone, for example, a gas, liquid, and solid. The degrees of freedom, F , are those externally controllable conditions of temperature, pressure, and composition, which are independently variable and which must be specified in order to completely define the equilibrium state of the system.

The derivation of the Gibbs phase rule is described in various texts on thermodynamics of materials (Ref 2–6). In the simple case of a pure metal (where $C = 1$), composition is a constant, while there could be two degrees of freedom if both temperature and pressure are allowed to change *while staying in equilibrium*. In this case ($C = 1$ and $F = 2$), then only one coexisting phase ($P = 1$) would be possible from the phase rule: $P = 1 - 2 + 2 = 1$. However, the phase rule also can define equilibrium conditions for multiple coexisting phases in a pure metal. For example, if pressure is held constant, then temperature is the only variable ($F = 1$). In this case, the phase rule predicts two coexisting phases in equilibrium: $P = 1 - 2 + 2 = 2$. In this case, the two phases occur when a pure metal is in the *thermal plateau* region that occurs during melting, solidification, or allotropic transformation of a pure metal.

The Gibbs phase rule also defines unique and constant conditions (referred to as *invariant points* in phase diagrams) where the maximum number of phases can coexist *while still in equilibrium*. Invariant points refer to equilibrium conditions when composition, pressure, and temperature must all remain constant ($F = 0$). In the case of a pure metal, for example, there is a unique and constant invariant point with three coexisting phases according to the phase rule: $P = 1 - 0 + 2 = 3$. This occurrence of three coexisting phases of a pure metal refers to the unique and constant *triple point* of the metal, which occurs at a very specific combination of pressure and temperature unique to a metal.

The phase rule also applies to alloys with any number of independent chemical components (C). The components, C , are the smallest number of substances of independently variable composition making up the system. In alloy systems, it is usually sufficient to count the number of elements present. In the case of a

mixture of stable compounds, such as salt and water, the number of components may be taken as two ($\text{NaCl} + \text{H}_2\text{O}$), unless the mixture is carried to a degree of temperature and pressure where one or both of the compounds decompose, when it becomes necessary to consider four components (Na , Cl , H , and O).

For most practical applications of the phase rule used in materials science, pressure is kept constant, and the number of degrees of freedom is reduced by 1, so that:

$$P = C - F \quad (\text{at constant pressure}) + 1 \quad (\text{Eq 6})$$

In this case, the only variables of the system would be the change in chemical concentration and/or temperature. In a binary alloy ($C = 2$), both composition and temperature could be variables during equilibrium, so that $F = 2$. In this case, the maximum number of heterogeneous phase equilibria would be: $P = 2 - 2 + 1 = 1$. Just one homogeneous phase would be possible, if both composition and temperature could vary while the system stays in equilibrium.

However, if equilibrium in a binary alloy can be maintained while either composition or temperature remains constant ($F = 1$), then two heterogeneous phases can exist in equilibrium: $P = 2 - 1 + 1 = 2$. This possible coexistence of two phases in a binary system represents phase regions such as the mushy zone (liquid + solid phases) or a two-phase mixture in a solid (such as the ferrite-austenite region of the iron-carbon system, Fig. 5). Phase diagrams of binary alloys also can have an invariant point (where $F = 0$), such that equilibrium conditions are defined by a specific (constant) composition and temperature. In this case, three coexisting phases ($P = 2 - 0 + 1 = 3$) occur for the invariant point

of a binary alloy. Examples of invariant point binary phase diagrams include:

- Eutectic points at a specific composition and temperature, where the liquid phase coexists with two different solid phases (three phases total in equilibrium)
- Eutectoid points at a specific composition and temperature, where three different solid phases can coexist in equilibrium (three phases total in equilibrium)

The iron-carbon system is the best example of a eutectoid system.

Theorem of Le Châtelier and the Clausius-Clapeyron Equation

Although the phase rule tells what lines and fields should be represented on a phase diagram, it does not usually define their shapes or the directions of the lines. Further guidance in the latter respect may be explained by several additional thermodynamic rules.

The theorem of Le Châtelier says that if a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction takes place that opposes the constraint, that is, one by which its effect is partially annulled. Therefore, if an increase in the temperature of an alloy results in a phase change, that phase change will be one that proceeds with heat absorption, or if pressure applied to an alloy system brings about a phase change, this phase change must be one that is accompanied by a contraction in volume.

The usefulness of this rule can be shown by reference to Fig. 8. Consider the line showing freezing, which represents for a typical pure metal the temperature at which melting occurs at various

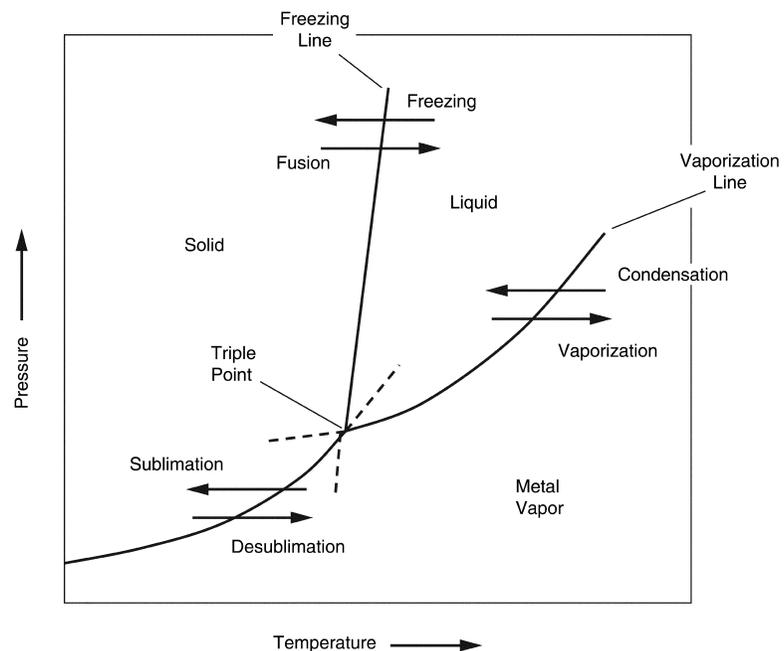


Fig. 8 Pressure-temperature diagram for a pure metal. Source: Ref 10

pressures. This line slopes upward away from the pressure axis. The typical metal contracts on freezing. Hence, applying an increased pressure to the liquid can cause the metal to become solid, experiencing at the same time an abrupt contraction in volume. Had the metal bismuth, which expands on freezing, been selected as an example, the theorem of Le Châtelier would dictate that the solid-liquid line be drawn so that the conversion of liquid to solid with pressure change would occur only with a reduction in pressure; that is, the line should slope upward toward the pressure axis.

A quantitative statement of the theorem of Le Châtelier is found in the Clausius-Clapeyron equation. Referring again to Fig. 8, this equation leads to the further conclusion that each of the curves representing two-phase equilibrium must lie at such an angle that on passing through the point of three-phase equilibrium, each would project into the region of the third phase. Thus, the sublimation-desublimation line must project into the liquid field, the vaporization curve into the solid field, and the solid-liquid curve into the vapor field.

The Lever Rule

The lever rule is one of the cornerstones of understanding and interpreting phase diagrams. A portion of a binary phase diagram is shown in Fig. 9. In this diagram, all phases present are solid phases. There are two single-phase fields labeled α and β , separated by a two-phase field labeled $\alpha + \beta$. It indicates that, at a temperature such as b , pure metal A can dissolve metal B in any proportion up to the limit of the single-phase α field at composition a . At the same temperature, metal B can dissolve metal A in any

proportion up to composition c , which, at this temperature, is the boundary of the single-phase β field. Therefore, at temperature b , any alloy that contains less than $a\%$ of metal B will exist at equilibrium as the homogeneous α solid solution; and any alloy containing more than $c\%$ of metal B will exist as the β solid solution. However, any alloy whose overall composition is between a and c (e.g., at d) will, at the same temperature, contain more metal B than can be dissolved by the α and more metal A than can be dissolved by the β . It will therefore exist as a mixture of α and β solid solutions. At equilibrium, both solid solutions will be saturated. The composition of the α phase is therefore $a\%$ of metal B and that of the β phase is $c\%$ of metal B .

When two phases are present, as at composition Y in Fig. 9, their relative amounts are determined by the relation of their chemical compositions to the composition of the alloy. This is true because the total weight of one of the metals, for example metal A , present in the alloy must be divided between the two phases. This division can be represented by:

$$W_0 \left(\frac{\%A_0}{100} \right) = W_\alpha \left(\frac{\%A_\alpha}{100} \right) + W_\beta \left(\frac{\%A_\beta}{100} \right)$$

$$\left(\begin{array}{l} \text{weight of metal} \\ A \text{ in alloy} \end{array} \right) = \left(\begin{array}{l} \text{weight of metal} \\ A \text{ in } \alpha \text{ phase} \end{array} \right) + \left(\begin{array}{l} \text{weight of metal} \\ A \text{ in } \beta \text{ phase} \end{array} \right) \quad (\text{Eq 7})$$

where W_0 , W_α , and W_β are the weights of the alloy, the α phase, and the β phase, respectively, and $\%A_0$, $\%A_\alpha$, and $\%A_\beta$ are the respective chemical compositions in terms of metal A . Because the weight of the alloy is the sum of the weight of the α phase and the weight of the β phase, the following relationship exists:

$$W_0 = W_\alpha + W_\beta \quad (\text{Eq 8})$$

This equation can be used to eliminate W_α from Eq 7, and the resulting equation can be solved for W_β to give the expression:

$$W_\beta = W_0 \left(\frac{\%A_0 - \%A_\alpha}{\%A_\beta - \%A_\alpha} \right) \quad (\text{Eq 9})$$

Although a similar expression can be obtained for the weight of the α phase W_α , the weight of the α phase is more easily obtained by means of Eq 8.

Because the weight of each phase is determined by chemical composition values according to Eq 9, the tie-line ac shown in Fig. 9 can be used to obtain the weights of the phases. In terms of the lengths in the tie-line, Eq 9 can be written as:

$$W_\beta = W_0 \left(\frac{\text{length of line } da}{\text{length of line } ca} \right) \quad (\text{Eq 10})$$

where the lengths are expressed in terms of the numbers used for the concentration axis of the diagram. *The lever rule, or inverse lever rule, can be stated: The relative amount of a given phase is proportional to the length of the tie-line on the opposite side of the alloy point of the tie-line.* Thus, the weights of the two phases are such that they would balance, as shown in Fig. 10.

Using Eq 10, the weight of the β phase at composition Y in Fig. 9 is:

$$W_\beta = W_0 \left(\frac{40 - 25}{65 - 25} \right) = W_0(0.375) \quad (\text{Eq 11})$$

The percentage of β phase can be determined by use of:

$$\begin{aligned} \text{Percentage of } \beta \text{ phase} &= \left(\frac{W_\beta}{W_0} \right) 100 \\ &= \left(\frac{\%A_0 - \%A_\alpha}{\%A_\beta - \%A_\alpha} \right) 100 \quad (\text{Eq 12}) \end{aligned}$$

At composition Y the percentage of β phase is:

$$\% \beta \text{ phase} = \left(\frac{40 - 25}{65 - 25} \right) 100 = 37.5\% \quad (\text{Eq 13})$$

The percentage of α phase is the difference between 100% and 37.5%, or 62.5%.

Lines and Labels

Magnetic transitions (Curie temperature and Néel temperature) and uncertain or speculative boundaries are usually shown in phase diagrams as nonsolid lines of various types.

The components of metallic systems, which usually are pure elements, are identified in phase diagrams by their symbols. Allotropes of polymorphic elements are distinguished by small (lowercase) Greek letter prefixes.

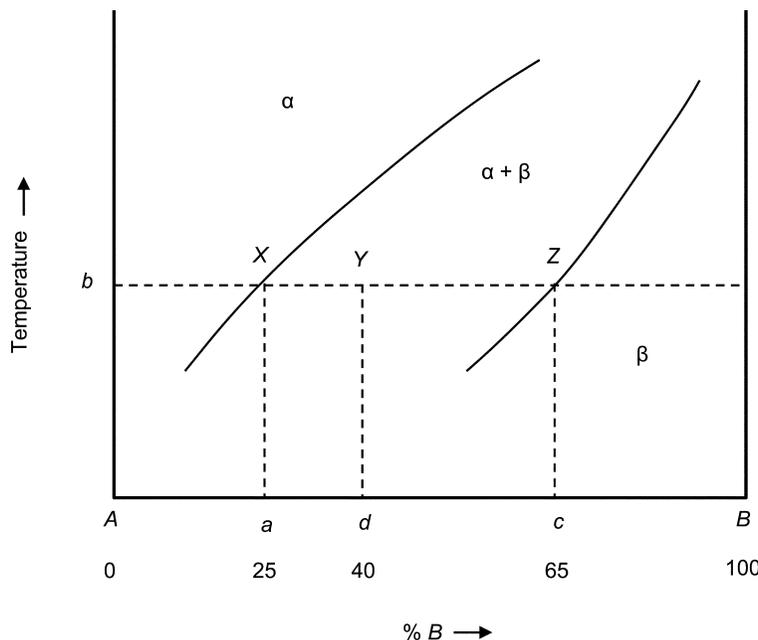


Fig. 9 Portion of hypothetical phase diagram. Source: Ref 11

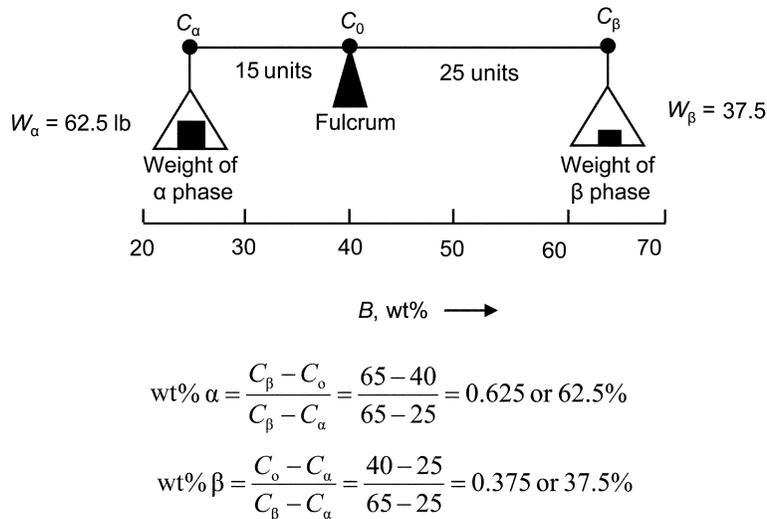


Fig. 10 Visual representation of lever rule. Source: Ref 11

Terminal solid phases are normally designated by the symbol (in parentheses) for the allotrope of the component element, such as (Cr) or (α Ti). Continuous solid solutions are designated by the names of both elements, such as (Cu, Pd) or (β Ti, β Y).

Intermediate phases in phase diagrams are normally labeled with small (lowercase) Greek letters. However, certain Greek letters are conventionally used for certain phases, particularly disordered solutions: for example, β for disordered bcc, ζ or ϵ for disordered close-packed hexagonal (cph), γ for the γ -brass-type structure, and σ for the σ CrFe-type structure.

For line compounds, a stoichiometric phase name is used in preference to a Greek letter (for example, A_2B_3 rather than δ). Greek letter prefixes are used to indicate high- and low-temperature forms of the compound (for example, αA_2B_3 for the low-temperature form and βA_2B_3 for the high-temperature form).

Application of Phase Diagrams

The use of phase diagrams in the application of typical alloy systems is discussed in separate articles based on the type or category of phase diagram. The different types of liquid-solid transformations are discussed in articles on:

- Isomorphous alloy systems
- Eutectic alloy systems
- Peritectic alloy systems
- Monotectic alloy systems

Application of phase diagrams also is instrumental in understanding solid-state transformations for the processing and heat treatment of alloys. The following sections provide brief introductions on various types of alloy systems that involve solid-state transformations. More details also are given in the article “Solid-State Transformations” in this Volume.

Iron-Carbon Phase Diagram

Steel and cast iron behavior are described in large part (but not exclusively) by the iron-carbon phase diagram. As noted, at standard pressure pure iron has three allotropic forms of solid iron and a magnetic phase transition at 770 °C (1420 °F). The addition of carbon introduces an additional degree of freedom and results in coexisting heterogeneous phases with several invariant points (Fig. 5) that include:

- A eutectic point at 4.30 wt% C and 1148 °C (2100 °F) where liquid phase coexists with austenite-carbon solid solution and cementite
- A eutectoid point at 0.77 wt% C at 727 °C (1340 °F) with three coexisting solid phases: austenite-carbon solid solution, ferrite-carbon solid solution, and cementite

Besides the occurrence of eutectic and eutectoid reactions, the formation of austenite at high temperatures is instrumental in the solid-state processing of steel. The fcc crystal structure of austenite is much more ductile than the bcc crystal structure of ferrite (because fcc crystals have more active slip systems than bcc crystals). Thus, hot working of steel is typically done at temperatures above the upper critical temperature (Ac_3) with complete austenitization (100% γ iron) of steel.

Carbon additions also lower the upper critical temperature (Ac_3) up to the eutectoid point of approximately 0.77 wt% C (Fig. 11). This allows for complete dissolution of cementite at lower temperatures and the subsequent manipulation of carbide formation during cooling. Dissolution of cementite can occur during heat treatment, because there is a great difference in the solid solubility of carbon in ferrite and austenite. The limit on solid solubility can be increased by raising the temperature to some extent, but carbon has very limited solubility

in a bcc matrix of α iron (Fig. 12), reaching a maximum of only 0.0218 wt% C at 727 °C. When carbon exceeds the solubility limit, the excess carbon combines with iron to form cementite (Fe_3C).

However, if the steel is heated above the upper critical temperature (Ac_3), the austenitic (fcc) phase can accommodate (dissolve) more carbon atoms than ferrite (α -phase) iron. The lattice spacing between atoms of γ iron is greater than that of α iron (Fig. 13), resulting in a higher solubility limit of carbon. Thus, when steel is heated above the Ac_3 temperature, the hard cementite phase (Fe_3C) dissolves into a solid solution of carbon in γ iron. Then by controlled cooling of the austenitic steel back down into the ferritic (α iron) phase, the morphology and distribution of iron-carbide phase (cementite) can be manipulated to produce a wide variety of microstructures and mechanical properties, as described in numerous publications.

However, it should also be mentioned that the iron-carbon equilibrium phase diagram is not a complete description of phase formation in steel. When austenitized steel is rapidly cooled (quenched), a different mechanism of phase transformation occurs. During rapid quenching from austenite to ferrite, there is not enough time for the excess carbon atoms to diffuse and form cementite along with the bcc ferrite. Therefore, some (or all) of the carbon atoms become trapped in the ferrite lattice, causing the composition to rise well above the 0.02% solubility limit of carbon in ferrite. This causes lattice distortion, so much so that the distorted bcc lattice rapidly transforms into a new metastable phase called martensite. Martensite does not appear as a phase on the iron-carbon equilibrium phase diagram because it is a metastable (nonequilibrium) phase that occurs from rapid cooling.

The unit cell of the martensite crystal is a body-centered tetragonal (bct) crystal structure, which is similar to the bcc unit cell, except that one of its edges (called the c axis) is longer than the other two axes (Fig. 14). The distorted form of the bct is a supersaturated phase that accommodates the excess carbon. The bct structure also occupies a larger atomic volume than ferrite and austenite, as summarized in Table 3 for different microstructural components as a function of carbon content. The density of martensite thus is lower than ferrite (and also austenite, which is denser than ferrite). The resulting expansion gives martensite its high hardness and is the basis for strengthening steels by heat treatment.

Binary Titanium Phase Diagrams with α and β Stabilizing Elements

Like iron, titanium is an allotropic element with two solid-state phases:

- α titanium with a hcp crystal structure at room temperature and up to 882 °C (1620 °F)
- β titanium with a bcc crystal structure that is stable from 882 °C up to the melting temperature